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PHYSICAL – CHEMICAL PHENOMENA OCCURRING DURING THE PRODUCTION OF SORBENT FROM A CLAY – DOLOMITE COMPOSITION

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It is found that in the production of a composite sorbent an acid – base interaction is observed between the Br?nsted centers on the surface of kaolinite and dolomite particles. During simultaneous dispersion the crystal structure of kaolinite is destroyed, which intensifies the interaction between the surface centers. It is shown that kaolinite plays a decisive role in the formation of the porous structure of granules and dolomite determines the strength of the articles produced.

Key words: liquids purification, sorbent, clay, dolomite, porous structure

The use of solid sorbents is one of the most widely method of purifying organic liquids. Natural bleached earths, based on aluminum silicate (kaolin and bentonite clays), are most widely used because they are easily available and inexpensive [1]. Sorbents in the form of granules are very promising for use in technology because in this case the purification process can be conducted in displacement apparatus in a continuous-flow regime.

A big drawback of granular sorbent obtained from clay is low mechanical strength, since it is undesirable to subject articles to high-temperature treatment. In this case, porosity decreases sharply, which is impermissible in the problem posed here. Thus, it is important to find an additive that can impart the required strength to granules without the sorbent being subjected to calcination. Another feature of the process of purifying organic liquids, in particular, vegetable and mineral oils, is that such liquids contain a substantial number of impurities with different chemical properties [2] — free fatty acids, peroxide compounds, heavy-metal cations, and others. To remove them the surface of the sorbent must also have different kinds of adsorption centers.

It is well known that kaolin clays on a surface characterize predominately Br?nsted acid centers [3]. To change the acid – base characteristics of a surface it is tempting to introduce into the sorbent a component with alkali properties [4]. On this basis dolomite can be such a component in our opinion. On the one hand, as a representative of carbonates of alkali-earth metals Ca and Mg, it possesses pronounced basic properties. On the other hand, when a water binder (dolomite) comes into contact with water at the preparation stage of the molding pastes, a large increase of the mechanical strength of granules should be expected to occur, making it possible to avoid high-temperature calcination.

Since clay and dolomite are natural raw materials, characterized by quite large particle sizes, there is no way to avoid comminution, which is quite energy-intensive, in the course of the preparation of the sorbent. In this connection the process can be conducted in two ways — the components can comminuted separately or in combination. It is well known [5] that these two mechanical treatment methods yield a product with different physical – chemical properties, which ultimately is what determines the operational parameters of the finished article.

Thus, our objective in the present work is to study the processes which occur during the preparation of granular sorbent from a composition consisting of kaolin clay + dolomite.

Dried clay from the Veselovskoe deposit and enriched dolomite from the Vladimir Oblast' were used as initial materials to prepare the sorbent granules. The initial materials were comminuted in a VM-4 vibrating roller-ring mill (vibration frequency 940 min^{-1}, energy intensiveness 5.4 kW/kg,

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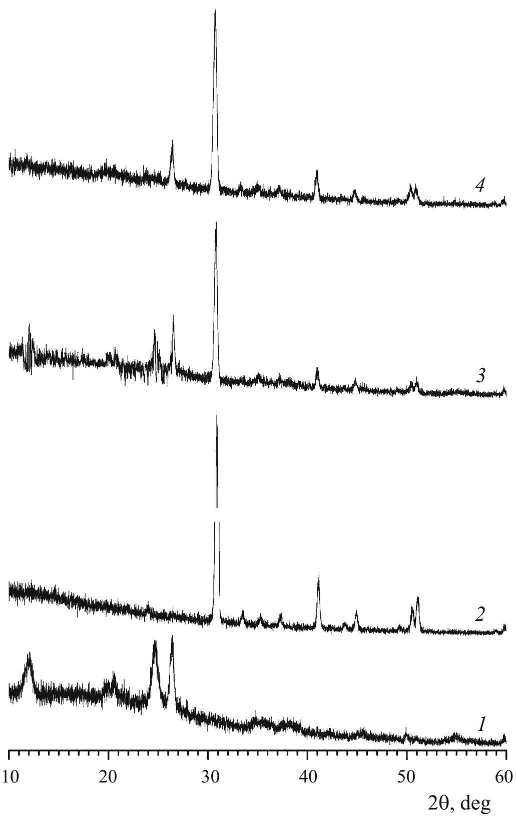

Fig. 1. X-ray diffraction pattern (CuK_α radiation) of clay (*1*), dolomite (*2*), clay and dolomite after separate comminution (*3*), and clay and dolomite after combined comminution (*4*).

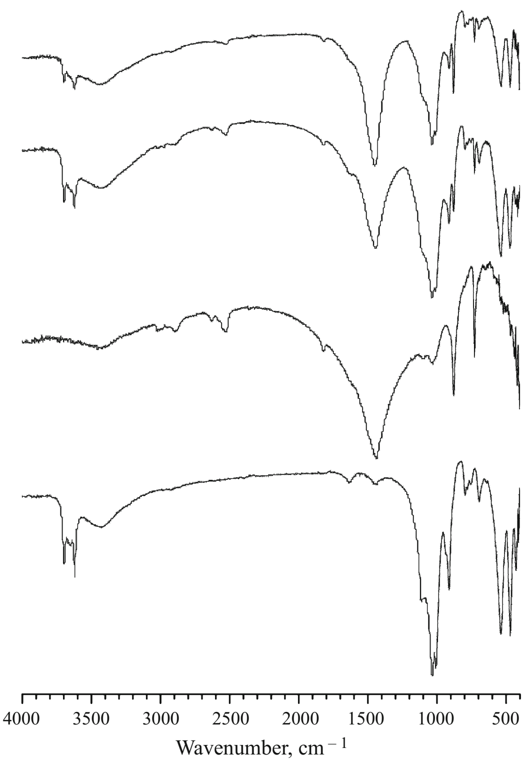

Fig. 2. IR transmission spectra of clay (*1*), dolomite (*2*), clay and dolomite after separate comminution (*3*), and clay and dolomite after combined comminution (*4*).

comminution time 60 min). The mass ratio of the components was 1 : 1. Distilled water served as the dispersion medium for preparing the molding pastes. The optimal molding moisture content was monitored according to the immersion depth of the cone of a P. A. Rebinder plastometer. According to the recommendations in [5], it was 28 – 30%. Cylindrical granules with diameter 4.5 mm and ratio $d/h = 1$ were obtained by plastic molding from a uniform paste using a piston extruder. The granules were dried in 6 h at 105 – 110°C to a constant mass.

A DRON-3M diffractometer with CuK_α radiation (wavelength 0.154 nm) was used to perform x-ray phase analysis. The "Avatar 360 FT-IR ESP" spectrometer system was used to obtain the IR transmission spectra. The granulometric composition was determined by dispersion analysis ("Fritisch Particle Sizer" apparatus). The differential distribution of the surface centers as a function of Hammett acidity was calculated from data obtained by potentiometric titration of 0.1 N solutions of HCl and NaOH, treated following the recommendations of [6]. The endface crushing strength of the granules as well as the density and porosity of the samples were determined by the methods of [7, 8].

The XPA data (Fig. 1) show that the Veselovskoe clay contains primarily kaolin (main peaks at diffraction angles $2\theta = 11.8$, 20.5, and 24.5°) and α quartz (main peak at diffraction angle $2\theta = 26.4°$) with montmorillonite and accompanying hydromicas as impurities. The IR spectrum of the sample has the characteristic form for kaolinite (Fig. 2) [3]. The characteristic absorption bands with wavenumbers near 1112 cm^{-1} (asymmetric stretching vibrations of Si – O) and 1033 and 1008 cm^{-1} (asymmetric stretching vibrations of octahedral layers of Al^{3+} with O^{2-} and OH^-) are clearly evident. Band splitting is observed in the region 3700 – 3600 cm^{-1}, corresponding to the stretching vibrations of the hydroxyl groups of the tops of the kaolinite octahedra. The appearance of a peak at 3696 cm^{-1} should be attributed to stretching vibrations of the internal hydroxyl groups and the peak at 3620 cm^{-1} to in-phase vibrations of paired surface hydroxyl groups [9].

The special structural features of kaolinite are responsible for the formation Br?nsted acid centers on the surface of the particles (Fig. 3). However, the distribution the basic centers does not have a pronounced peak.

After dry comminution of the clay in a vibrating mill the powder contains particles with predominate diameters 5 – 15 μm. The granulometric composition of the powders (Table 1) makes it possible to classify the system under study as a medium-dispersion system.

The x-ray diffraction pattern of dolomite powder from a deposit in Vladimir Oblast' is a copy of the diffraction pattern of double carbonate $CaMg(CO_3)_2$. The IR spectrum of

the sample likewise corresponds to the structure of dolomite, as the wide characteristic absorption band (peak at 1438 cm^{-1}), corresponding to asymmetric stretching vibrations of the carboxyl groups, attests. The presence in dolomite of alkali-earth cations Ca^{2+} and Mg^{2+} ensures a high concentration of basic centers on the surface of the particles. Data from the dispersion analysis of dolomite powder in a vibrating mill attest that its granulometric composition is close to that of comminuted clay; the 5 – 15 μm particle-size fraction predominates.

As expected, a mechanical mixture of separately comminuted clays and dolomite also gives a diffraction pattern and an IR spectrum which are obtained by adding some components or other taking account of their content. The content of fractions in the mixture likewise corresponds to the arithmetic-mean values. However, considerable changes were observed in the character of the distribution of the acid – base centers. Here, two groups can be identified as corresponding to the Hammett acidity ranges 6.8 – 7.1 and 9 – 11. The observed redistribution of the acid – base centers became possible during the preparation of the molding mix. Therefore it can be stated that interaction of surface centers of kaolinite and dolomite particles with a decrease of the acidity and basicity of the centers occurs on mixing in water, as the shift of the peaks as compared with the initial samples attests.

The sample prepared from a clay – dolomite composition subjected to combined comminution in a vibrating mill is of special interest. Reflections of only dolomite and quartz are seen in the diffraction pattern of the sample, and there are no peaks corresponding to kaolinite. The IR spectroscopic investigation of the sample shows that the characteristic absorption bands of kaolinite in the high- and low-frequency regions remain but their intensity decreases by a factor of approximately 2. This shows that the crystalline structure of kaolinite is destroyed when the clay and dolomite are comminuted together and that the kaolinite becomes x-ray amorphous. However, the valence bands characteristic for kaolinite, specifically, Si – O and Al – O(H), remain. We also call attention to the change in the granulometric composition of the powder after combined treatment of the composition in the comminution apparatus. Compared with the samples examined, the average size of the particles is larger and the 15 – 30 μm fraction predominates. In addition, the particle-size distribution becomes close to monodisperse.

These phenomena which occur after combined comminution can be explained by considering the hardness values of the crystals. The Mohs hardness is 1.5 – 2 for kaolinite, 3.5 – 4 for dolomite, and 7 for quartz. Thus, kaolinite is much softer than the other components of the composition and, moreover, it can be easily cleaved along a plane with Miller indices 001. Thus, for combined dry comminution, dolomite and quartz crystals are additional milling bodies with respect to $Al_2Si_2O_5(OH)_4$. As a result, kaolinite crystals not only cleave but they also plastically deform right up to complete amorphization of the structure.

TABLE 1.

Sample	Content, %, of fraction, μm				
	< 1	1 – 5	5 – 15	15 – 30	> 30
Clay	1.56	0.13	78.45	0.12	19.74
Dolomite	1.10	0.12	80.23	2.97	15.58
Clay and dolomite:					
separate comminution	1.33	0.13	79.34	1.54	17.66
combined comminution	0.62	1.63	1.80	94.70	1.25

As a result of the simultaneous presence of components with such a large difference of crystal hardness in the system, comminution intensifies the aggregation of solid-phase particles, which the strongly disordered and, correspondingly, more active kaolinite structure promotes. It is also possible that the softer component acts as a damping buffer between the dolomite and quartz particles, thereby impeding the fragmentation of the latter.

The processes described above also have a considerable influence on the surface properties of the composition. In the presence of intense destruction of the crystal structure of kaolinite, the acid – base interaction of the surface centers now occurs at the combined comminution stage. The subsequent introduction of water into the system intensifies this process, because proton transfer is facilitated. Such interaction results in an appreciable decrease of the acidity and basicity of the surface centers. This is indicated by the fact that a group of acid centers appears only at $H_0 = 7.2 – 7.5$, while basic centers appear at $H_0 = 8.8 – 9.5$ (see Fig. 3). A change of the surface properties once again underscores the increase of the chemical activity of the solid phase, especially of kaolinite, under an external mechanical impulse during the comminution process.

An examination of the physical properties of the granules (Table 2) shows that the sorbent prepared from clay possesses a low porosity against the background of very low mechanical strength. Conversely, the granules obtained from dolomite, being stronger, are characterized by a completely acceptable strength. It should also be noted that its open porosity (an important indicator for a sorbent) is more than 1.5 times greater. It was note previously that both clay and dolomite have a close fractional composition after comminution (see Table 1). The lower porosity of the clay sorbent indicates that the particles in this sample are more closely packed than the dolomite particles. An additional confirmation is the higher apparent density of the granules (see Table 2), especially considering that the true density of dolomite (2.84 g/cm^3) is somewhat greater than that of clay (2.60 g/cm^3).

It is known [5] that the strength of an article is determined by the number of contacts and the strength of each individual contact. As a result of close packing of the clay par-

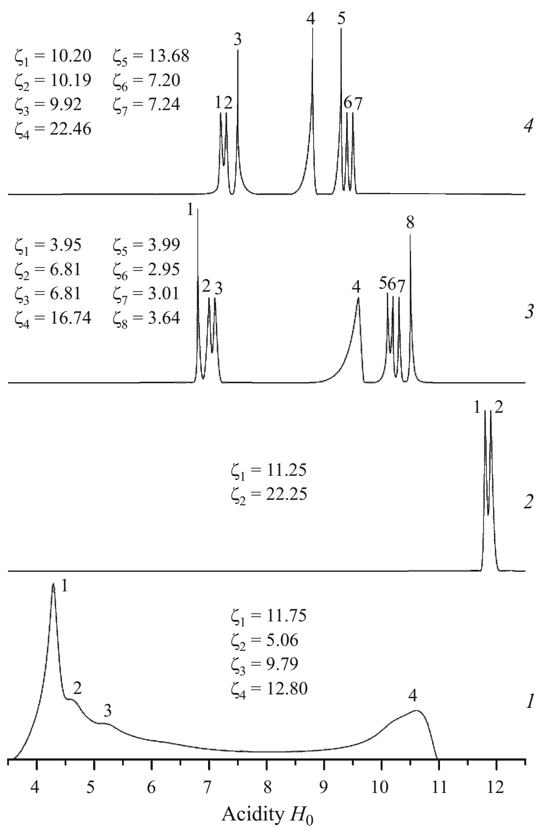

Fig. 3. Distribution of centers as a function of the Hammett acidity H_0 on the surface of the samples of clay (*1*), dolomite (*2*), clay and dolomite after separate comminution (*3*), and clay and dolomite after combined comminution (*4*): ζ_i) concentration of surface centers (μmole/g).

ticles, the number of contacts between the particles increases sharply. However, the strength of these contacts is considerably lower than for dolomite particles, as the corresponding characteristics of the granules obtained confirm.

An examination of the porous structure of a composition of clay and dolomite shows that kaolinite particles make the determining contribution to pore formation. The close values of the porosity and apparent density of the samples support this (see Table 2). It should be noted that the total porosity and open porosity of the granules increase after combined comminution of the components of the composition, since the average size of the agglomerates also increases in the present case (see Table 1). The crystallization contacts between the dolomite particles have a decisive effect on the strength indicators, since the strength of an article made from the composite material remains quite high.

In summary, when the powders are mixed with water, an acid – base interaction between the centers on the surface of the kaolinite and dolomite particles is observed because proton transfer is facilitated. This lowers the acidity of the Brönsted centers. It was found that the crystal structure of kaolinite, being the softest ingredient in the composition, is destroyed when clay and dolomite are comminuted together. In the process, the acid – base interaction between the surface centers intensifies in water. Kaolinite plays the main role in the formation of the porous structure of the granules, while the strength of the articles is determined by the crystallization bonds of dolomite.

TABLE 2.

Sample	Apparent density, g/cm^3	Total porosity, %	Open-pore volume, cm^3/g	Granule strength, MPa
Clay	1.87	26	0.088	1.0
Dolomite	1.75	37	0.147	3.0
Clay and dolomite:				
separate comminution	1.91	25	0.093	3.5
combined comminution	1.85	27	0.121	3.5

REFERENCES

1. M. P. Aznaur'yan and N. A. Kalasheva, *Modern Technologies for Purifying Fats and Production of Margarine and Mayonnaise* [in Russian], Khimiya, Moscow (1999).
2. P. B. Razgovorov, S. V. Sitanov, V. Yu. Prokof'ev, and K. V. Smirnov, "Prediction of the quality of wax removal from vegetable oils in the presence of white clay," *Khim. Rastit. Syr'ya*, **50**(6), 39 – 42 (2007).
3. P. B. Razgovorov, "Infrared spectra of systems based on activated kaolin," *Izv. Vyssh. Uchebn. Zaved., Ser. Khim. Khim. Tekhnol.*, **50**(6), 39 – 42 (2007).
4. V. Yu. Prokof'ev, P. B. Razgovorov, K. V. Smirnov, et al., "Extrusion formation of kaolin-based sorbents," *Steklo Keram.*, No. 8, 29 – 32 (2007).
5. A. P. Il'in and V. Yu. Prokof'ev, *Physical – Chemical Mechanics in the Technology of Catalysts and Sorbents* [in Russian], Izd. IGKhTU, Ivanovo (2004).
6. A. P. Golikov, "Method for calculating the acid-base characteristics of a sorbent from the results of potentiometric titration," *Zh. Fiz. Khim.*, **69**(4), 664 – 667 (1995).
7. E. D. Shchukin, A. I. Bessonov, and S. A. Paranskii, *Mechanical Tests of Catalysts and Sorbents* [in Russian], Nauka, Moscow (1971).
8. D. N. Poluboyarinov and R. Ya. Popil'skii (eds.), *Study with Experimental Work of the Technology of Ceramics and Refractories* [in Russian], Stroiizdat, Moscow (1972).
9. S. Olejnik, A. M. Posner, and I. P. Quirk, "Infrared spectrum on the kaolinite-pyridine N-oxide complex," *Spektrochim. Acta*, **27**(9), 2005 – 2009 (1971).